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Authors

Guo, H
Ding, AJ
Wang, T
et al.

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Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pearl River Delta region, southern China

H. Guo,[1] A. J. Ding,[1] T. Wang,[1] I. J. Simpson,[2] D. R. Blake,[2] B. Barletta,[2] S. Meinardi,[2] F. S. Rowland,[2] S. M. Saunders,[3] T. M. Fu,[1] W. T. Hung,[1] and Y. S. Li[1]

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[1] We analyze 16-month data of 13 major halocarbons measured at a southern China coastal site in the greater Pearl River Delta (PRD). A total of 188 canister air samples were collected from August 2001 to December 2002. Overall inspection indicated that CH_2Cl_2, C_2Cl_4, and C_2HCl_3 had similar temporal variations while CFC-11, CFC-12, and CFC-113 showed the same emission patterns during the sampling period. Diurnal variations of halocarbons presented different patterns during ozone episode days, mainly related to emission strength, atmospheric dispersion, and photochemical lifetimes. For further statistics and source appointment, Lagrangian backward particle release simulations were conducted to help understand the potential source regions of all samples and classify them into different categories, including local Hong Kong, inner PRD, continental China, and marine air masses. With the exception of HCFC-142b, the mixing ratios of all halocarbons in marine air were significantly lower than those in urban and regional air ($p < 0.01$), whereas no significant difference was found between urban Hong Kong and inner PRD regional air, reflecting the dominant impact of the greater PRD regional air on the halocarbon levels. The halocarbon levels in this region were significantly influenced by anthropogenic sources, causing the halocarbon mixing ratios in South China Sea air to be higher than the corresponding background levels, as measured by global surface networks and by airborne missions such as Transport and Chemical Evolution Over the Pacific. Interspecies correlation analysis suggests that $CHCl_3$ is mainly used as a solvent in Hong Kong but mostly as a feedstock for HCFC-22 in the inner PRD. Furthermore, CH_3Cl is often used as a refrigerant and emitted from biomass/biofuel burning in the inner PRD. A positive matrix factorization receptor model was applied to the classified halocarbon samples in the greater PRD for source profiles and apportionments. Seven major sources were identified and quantified. Emissions from solvent use were the most significant source of halocarbons (71 ± 9%), while refrigeration was the second largest contributor (18 ± 2%). By further looking at samples from the inner PRD and from urban Hong Kong separately, we found that more solvent was used in the dry cleaning industry in Hong Kong, whereas the contribution of cleaning solvent in the electronic industry was higher in the inner PRD. Besides the two common sources of solvent use and refrigeration, the contributions of biomass/biofuel burning and feedstock in chemical manufacturing was remarkable in the inner PRD but negligible in Hong Kong. These findings are of help to effectively control and phase out the emissions of halocarbons in the greater PRD region of southern China.

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1. Introduction

[2] Halogenated hydrocarbons (halocarbons) are unique air contaminants in the atmosphere, in part because of their persistence. Unlike most nonmethane hydrocarbons (NMHCs), the atmospheric lifetimes of halocarbons range from months to decades [*Warneck*, 2000]. Important halocarbons include (1) solely chlorinated hydrocarbons that with the exception of carbon tetrachloride (CCl_4), are short-lived, (2) long-lived fluorinated and fully halogenated hydrocarbons such as CFCs, and (3) replacements for CFCs (e.g., HCFCs) with shorter but still reasonably long lifetimes

[1]Department of Civil and Structural Engineering, Hong Kong Polytechnic University, Kowloon, Hong Kong.
[2]Department of Chemistry, University of California, Irvine, California, USA.
[3]School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, Perth, Western Australia, Australia.

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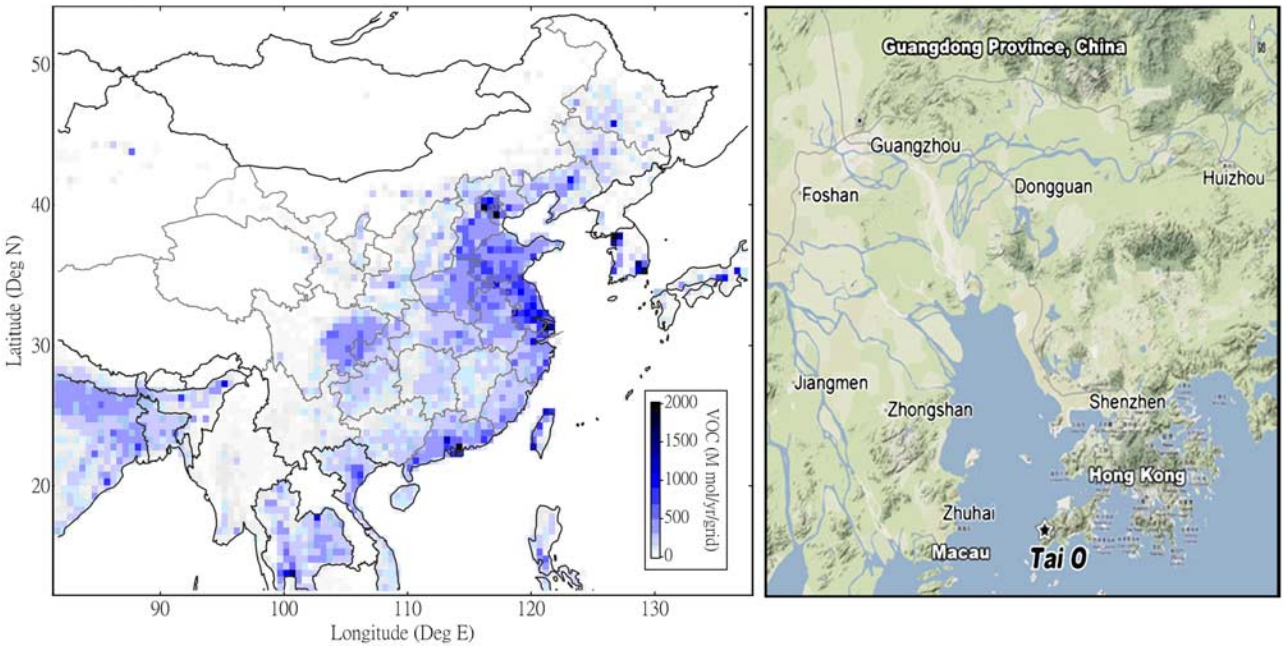

Figure 1. Map showing (right) the study site and Pearl River Delta of China and (left) emission inventory of anthropogenic NMVOC (30 lumped species for SAPRC99 mechanism, unit: M mol/a per 0.5° × 0.5°grid. Data were obtained from http://www.cgrer.uiowa.edu/EMISSION_DATA_new/index_16.html).

[*Brasseur et al.*, 1999; *Seinfeld and Pandis*, 2006]. As a result of their important industrial and commercial properties such as low reactivity, low toxicity, thermal absorption, and solvent properties, CFCs, HCFC-22, HCFC-141b, and HCFC-142b are often used as aerosol propellants, refrigerants, degreasing solvents and foam blowing agents [*Aucott et al.*, 1999; *McCulloch et al.*, 2001, 2003]. Since CFCs have no tropospheric sink, they can be photolytically destroyed to yield free Cl and F by UV light in the stratosphere, and subsequently the free Cl catalytically destroys stratospheric ozone [*Molina and Rowland*, 1974]. The very low reactivity also allows chlorofluorocarbons to survive unchanged in most commercial applications and eventually to be released to the atmosphere in their original gaseous form [*Seinfeld and Pandis*, 2006]. These same CFCs are potentially important greenhouse gases that efficiently absorb infrared radiation [*Hofmann et al.*, 2006]. Because of their responsibility for ozone depletion, these halocarbons have been phased out or controlled in developed countries under the Montreal Protocol and its amendments (http://www.theozonehole.com/montreal.htm). On the other hand, though they are not regulated by the Montreal Protocol because of their low impact on stratospheric ozone, halocarbons such as CH_2Cl_2, C_2HCl_3 and C_2Cl_4 are hazardous and toxic organic compounds in regional air quality inventories [*Simmonds et al.*, 2006].

[3] The Pearl River Delta (PRD) is a dynamic region on the southern coast of China that has become distinguished for its rapid industrial development and thriving economy. The greater PRD region consists of nine cities within Guangdong Province, i.e., Guangzhou, Shenzhen, Zhuhai, Dongguan, Zhongshan, Foshan, Jiangmen, Huizhou, and Zhaoqing (usually these nine cities are considered to comprise the inland PRD region), plus Hong Kong and Macau Special Administrative Regions, as shown in Figure 1. The greater PRD's industries manufacture a wide variety of goods from electronics and air conditioners to refrigerators and automobiles. A consequence of the rapid industrialization and urbanization is the deterioration of air quality in this region. Indeed, studies have evidenced high levels of ozone and its precursors, and low visibility on the regional scale [*Wang and Kwok*, 2003; *Wang et al.*, 2005; *Streets et al.*, 2006; *Zhang et al.*, 2008; *Wang et al.*, 2008]. Emissions of halocarbons in this region and in China as a whole have also attracted the international attention because China is an "Article 5" party. That is, China is a developing country still allowed to produce CFCs, halons, and other halocarbons under the terms of the Montreal Protocol and its amendments. *Blake et al.* [2003] and *Palmer et al.* [2003] characterized halocarbon emissions from China using Transport and Chemical Evolution Over the Pacific (TRACE-P) and Pacific Exploratory Mission–west B aircraft measurement data. Recently, *Barletta et al.* [2006] reported ambient halocarbon mixing ratios in 45 Chinese cities. *Chan and Chu* [2007] studied ambient halocarbons in 2000 in the industrial-related atmosphere of the inland PRD. Significant enhancement of most halocarbons was found in this region because of their increased production and extensive industrial uses. However, all these studies were focused on characterizing chemical speciation and abundance of Asian continental outflow and polluted air masses affected by industrial sources. The source origins, source profiles and source apportionment of halocarbons in the region remain more poorly studied. Thus, to effectively control and phase out the emissions of halocarbons, it is essential to determine their source regions and the source contributions to the halocarbons in this region.

[4] Receptor-oriented source apportionment models are useful tools to identify sources of ambient air pollutants and to quantitatively estimate source contributions to air

pollutants through statistical interpretation of ambient measurements and additional imposed constraints. One of the receptor models is positive matrix factorization (PMF). The PMF provides a flexible modeling approach that can effectively use the information contained within the air sample data. Details about the PMF model are described by *Paatero and Tapper* [1993, 1994] and *Paatero* [1997].

[5] PMF uses a least squares approach to solve the factor analysis problem by integrating nonnegative constraints into the optimization process and utilizing the error estimates for each data value as point-by-point weights [*Li et al.*, 2004]. PMF has been widely applied to a number of aerosol studies in the United States including urban locations [e.g., *Ramadan et al.*, 2000; *Maykut et al.*, 2003; *Kim and Hopke*, 2004], and rural and remote locations [e.g., *Polissar et al.*, 1998, 2001; *Poirot et al.*, 2001]; in Europe [e.g., *Yli-Tuomi et al.*, 1996; *Qin and Oduyemi*, 2003]; and in Asia [e.g., *Lee et al.*, 1999; *Sun et al.*, 2004]. In addition to the above aerosol application, the PMF model has been applied to volatile organic compounds [e.g., *Zhao et al.*, 2004; *Kim et al.*, 2005]. Profiles and contributions of particulate matter and volatile organic compounds from primary sources, such as vehicular emissions, fuel combustion, biomass burning and sea salt are typically identified by PMF modeling in these studies.

[6] A comprehensive field measurement campaign was carried out at a polluted rural/coastal site in the PRD from August 2001 to December 2002, in order to understand the photochemical smog problem in this region. Using this data set, the causes of a multiday ozone episode were analyzed [*Wang and Kwok*, 2003], the temporal variability and emission patterns of pollution plumes during October–December 2001 were characterized [*Wang et al.*, 2003], and the seasonal profiles and atmospheric processes of trace gases (including NMHCs) were overviewed [*Wang et al.*, 2005]. C_1–C_5 alkylnitrates and their relation to their parent NMHCs and to ozone were also examined [*Simpson et al.*, 2006], and the regional and local source contributions to NMHCs were quantified using PCA/APCS receptor model [*Guo et al.*, 2006] and by chemical ratios [*Zhang et al.*, 2008]. Here, we mainly analyze the halocarbon data collected during the sampling periods. The source origins and spatiotemporal variations of halocarbons will be discussed, and source profiles of major local and regional sources and their contributions to ambient halocarbons will be quantified. To our best knowledge, this is the first time source profiles of halocarbons in south China have been obtained. The findings extracted in this study are expected to help understand the usage patterns, emissions and controls of halocarbons in the greater PRD region.

2. Experimental Section

2.1. Sampling Site

[7] The sampling site, Tai O, was located in a rural/coastal area on the western coast of Lantau Island in southwest Hong Kong (22.25°N, 113.85°E) (Figure 1). A detailed description of the site is provided by *Wang et al.* [2003]. In brief, Tai O site is about the same distance (32 km) to the west of the Hong Kong urban center and to the east of Macau. The three largest population centers in the PRD are Guangzhou (10 million), Hong Kong (6.9 million) and Shenzhen (4 million). The power plants, airports and seaports are mainly located along the two sides of the Pearl Estuary.

[8] The study site is located on a hill 80 m above sea level, overlooking the Pearl Estuary to the west and north, the South China Sea to the south, and the Hong Kong urban center to the east. There are small local anthropogenic emissions due to a sparse population and light traffic at Tai O. Many deciduous trees, sources of biogenic trace gases, are immediately surrounding the site. The site is characterized by prevailing northeasterly winds in the winter when it is frequently impacted by urban pollution plumes originating from PRD, including Hong Kong, and by southerly winds during summer when the site receives cleaner air from the tropical Pacific Ocean and South China Sea.

2.2. Sampling and Chemical Analysis

[9] Whole air samples were pressurized to about 20 psi into evacuated 2-L electro-polished stainless steel canisters using a metal bellows pump. The canisters were cleaned and evacuated at the University of California, Irvine (UCI) before being shipped to Tai O. Details of the preparation and preconditioning of the canisters are described by *Blake et al.* [1994]. During sampling the canister valve was slightly opened, allowing about one minute for the collection of the "integrated" air samples. The canisters were then shipped to UCI for chemical analysis. A six-column multiple GC-MS system was used to identify and quantify volatile organic compounds. In general, the precision of the halocarbon measurements varies compound by compound, and is 1–2% for CFCs, 2–4% for HCFCs, and 1–4% for the other halocarbons (except 5% for CH_2Cl_2). The measurement accuracy also varies compound by compound, and is 2% for CFCs, 5% for $MeCCl_3$, CCl_4, CH_3Cl and CH_3Br, and 10% for the other halocarbons. Detailed descriptions of the chemical analysis, relevant quality assurance/quality control, and the measurement precision and accuracy for each species are given by *Colman et al.* [2001].

[10] Between August 2001 and December 2002, a total of 188 canister samples were taken. The number of samples collected each month varied from 1 to 32. Most of the air samples were acquired between August and December because of the highest frequency of poor air quality days during this period [*Wang et al.*, 2003, 2005]. All samples were collected in the daytime, when factories were under normal operation, with 75% of the samples taken in the afternoon and 25% in the midmorning.

[11] Additionally, O_3, CO, SO_2, NO, and NO_y were continuously measured during the study period. Several meteorological parameters were simultaneously monitored at Tai O, including wind speed, wind direction, temperature, relative humidity, total ultraviolet radiation (320–400 nm), and global solar radiation.

2.3. Lagrangian Particle Release Simulation and Air Mass Classification

[12] To help understand the air mass history, we conducted backward Lagrangian particle release simulations for all samples, using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT4, Version 4.8), which is developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (http://www.arl.noaa.gov/ready/hysplit4.html). The model was run in a 7-day backward mode with total 2000 particles released at 200 m above the site. For the calculation of particle dis-

persion, a 3-D method was adopted. The meteorological data that drove the model were from the GDAS data set (3 hourly, global, 1° in longitude and latitude, and 23 pressure levels) (see http://www.arl.noaa.gov/ss/transport/gdas1.html for details). A similar methodology has been previously applied by *Zhang et al.* [2009].

[13] Different from the traditional trajectory method, the backward particle release simulation, including the dispersion processes related to turbulence mixing, provides more accurate information about the history of air masses [*Ding et al.*, 2009; *Zhang et al.*, 2009]. For the simulation of each sample, the air mass concentration, i.e., the normalized residence time, at the altitude 100 m above ground level were calculated for a further analysis. Here the lowest 100 m thickness was considered as the "footprint" retroplume layer, which is easily affected by surface emissions [*Stohl et al.*, 2003; *Ding et al.*, 2009]. With the sum of footprint air mass concentrations, all samples are classified into four major categories: HK, Hong Kong local air; inner PRD, air masses from the PRD except Hong Kong; RgC, regional air from continental China; and MA, marine air mass from the South China Sea or the Pacific. For inner PRD and HK categories, we summed the air masses concentrations (i.e., residence time) within the two geographical boundaries (see white line in Figures 2a and 2b) and identified each sample on the basis of a criterion that the total concentration was higher than one mean plus one standard deviation. Using this method, 27 and 23 samples were classified into Categories HK and inner PRD. Since previous studies [e.g., *Ding*, 2004; *Guo et al.*, 2009] showed that the air masses in Hong Kong mostly come from the eastern and southeastern Chinese mainland, we identified these air masses with a criterion that the total land residence time was higher than the median land residence time; that is, the highest 50% (95 samples) were selected. It should be noted that using these methods, some samples were duplicately classified into the three categories. The total number for the three categories of air masses with anthropogenic influences was 112. We use these samples for a further source apportionment analysis later. For the MA category, we selected 19 samples (i.e., about 10% of total samples) on the basis of the value of summed marine residence time. The residual 57 samples, which were relatively well mixed with various air masses, were not included in the statistics in this paper.

[14] To investigate the difference in the potential source regions and to see how well our classification method works, in Figures 2a–2d we show the distribution of the averaged footprint air mass concentrations for the four categories: inner PRD, HK, RgC and MA, respectively. For the first two categories, the results are presented in a small region with higher resolution. It can be clearly seen that using the above mentioned method, the potential source regions agree very well with our previous definitions. It also indicates the sample numbers of all categories, from perspective of transport, are statistically representative. For example, the marine (MA) and regional air mass (RgC) patterns were similar to the climatological results from 10-year back trajectory analysis [*Ding*, 2004]; and the inner PRD air covered different areas of the greater PRD region, so did the Hong Kong air masses.

2.4. PMF Receptor Model

[15] The PMF was used to resolve the halocarbons data obtained at Tai O in the greater PRD region. Briefly, a mass balance equation can be written to account for all m chemical species in the n samples as concentrations from p independent sources:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \tag{1}$$

where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} is the species contribution of the kth source to the ith sample, f_{kj} is the jth species fraction from the kth source, e_{ij} is residual associated with the jth species concentration measured in the ith sample, and p is the total number of independent sources [*Paatero*, 1997]. PMF provides a matrix of the source profiles and a matrix of the time series of source contributions without prior knowledge of halocarbon sources. In PMF, sources are constrained to have nonnegative species values, and no sample can have a negative source contribution. An "object function," Q, that is to be minimized as a function of G and F is given by:

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left[\frac{e_{ij}}{s_{ij}}\right], \tag{2}$$

where s_{ij} is an estimate of the "uncertainty" in the jth variable measured in the ith sample. The factor analysis problem is then to minimize Q(E) with respect to G and F with the constraint that all of the halocarbons of G and F are to be nonnegative. PMF uses a unique algorithm in which both G and F matrices are varied simultaneously in each least squares step. The algorithm was described by *Paatero* [1997].

[16] The application of PMF depends on the estimated uncertainties for each of the measured data. The uncertainty estimation provides a useful tool to decrease the weight of missing and below detection limit data in the solution. *Polissar et al.* [1998] provided a set of guidelines for estimating the input uncertainties. By this method, the concentration values were used for the measured data, and the sum of the analytical uncertainty plus 1/3 of the detection limit value was used as the overall uncertainty assigned to each measured value. Values below the detection limit were replaced by half of the detection limit values and their overall uncertainties were set at 5/6 of the detection limit values. Missing values were replaced by the geometric mean of the measured values and their accompanying uncertainties were set at four times of this geometric mean value [*Li et al.*, 2004; *Kim et al.*, 2005].

[17] To find the number of sources and their profiles, it is necessary to test different numbers of sources and find the optimal value with the most physically reasonable results. The results of the PMF analyses are not hierarchical; that is, a higher-dimension solution does not necessarily contain all the factors of the lower dimensions. Thus, different numbers of factors were tested, and an optimum solution was determined on the basis of both a good fit to the data and the most meaningful results. If the number of sources is estimated properly, the theoretical value of Q should be approximately equal to the number of degree of freedom, or approximately equal to the total number of data points. However, if the

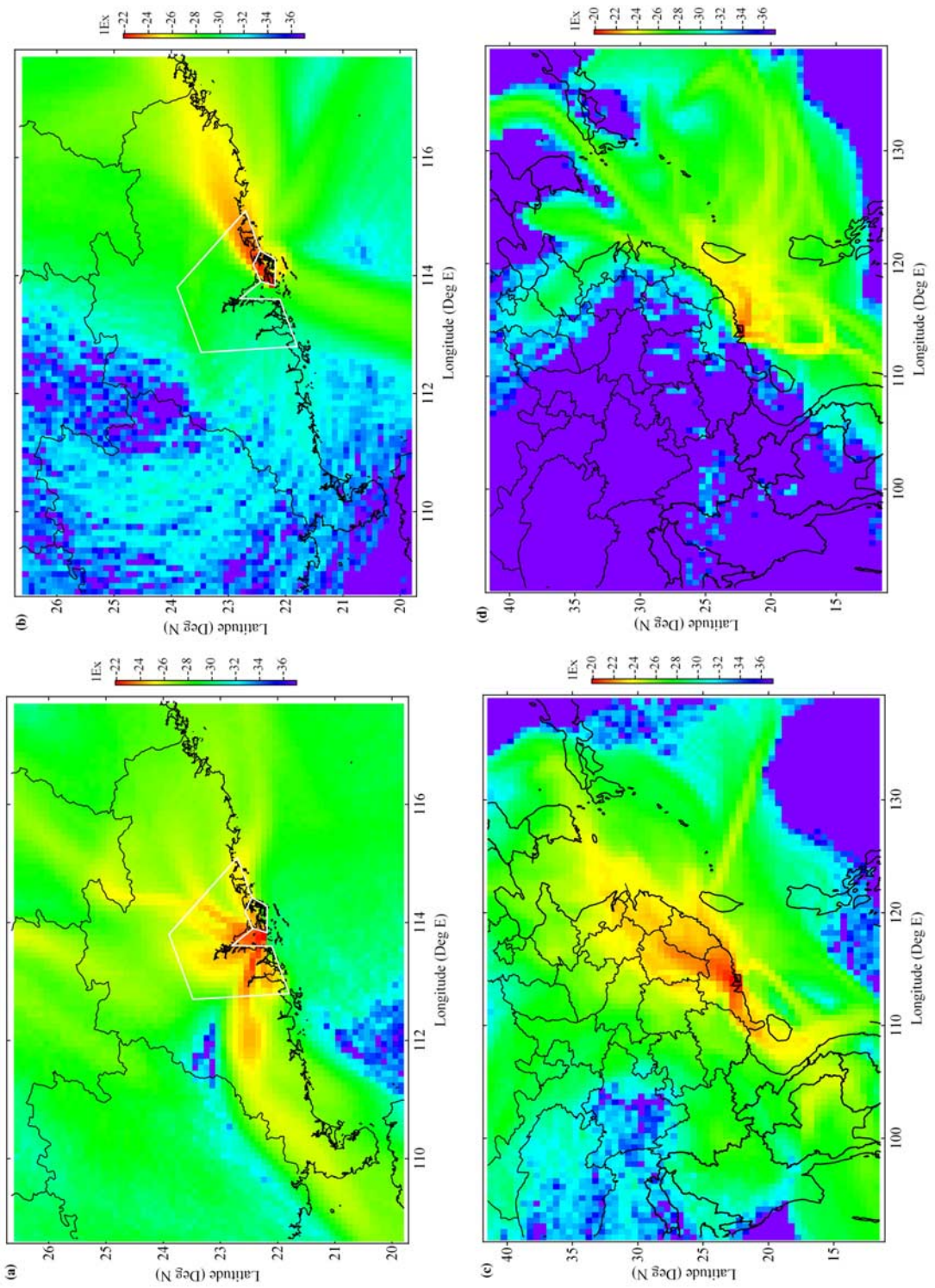

Figure 2. Distribution of air mass concentrations (in unit of mass/m^3 h) within surface 100 m from HYSPLIT Lagrangian backward particle release simulation, showing the potential source regions, for the four air mass categories: (a) inner PRD, (b) HK, (c) RgC, and (d) MA.

number of sources is not well determined, the value of Q may deviate from the theoretical value.

3. Results and Discussion

3.1. General Features

3.1.1. Daily Patterns of Halocarbons

[18] In order to understand the temporal patterns of main halocarbon species in the region, the time series of the halocarbons measured from August 2001 to December 2002 is plotted (Figure 3). It shows that the summer values of the halocarbons were generally lower than those in autumn and winter seasons. This pattern has been evidenced by other gaseous primary pollutants and nonmethane hydrocarbons because of the influence of Asian monsoon circulations, OH radical seasonality, and boundary layer height [*Wang et al.*, 2005].

[19] It can be seen that CH_2Cl_2, C_2Cl_4 and C_2HCl_3 had similar temporal variations during the 16-month sampling period, suggesting that they might be originated from the same source or be used in the same pattern or have similar sink reactions and behavior (Figure 3a). CH_2Cl_2, C_2Cl_4 and C_2HCl_3 have applications in the industrial sector mainly as solvents and degreasers [*Sturrock et al.*, 2002; *Simmonds et al.*, 2006], and their photochemical lifetimes are similar (2–5 months, Table 1).

[20] Similar temporal patterns are found for CFC-11, CFC-12, and CFC-113, suggesting the same source or concurrent use or similar sink behavior of these CFCs (Figure 3b). As is known, CFCs are mainly used as refrigerants in cooling appliances and air conditioning, as foam blowing agents, and as aerosol propellants [*Aucott et al.*, 1999; *McCulloch et al.*, 2001, 2003]. In addition, CFC-11 together with CFC-113 is used as degreasers in the cleaning process for the production of refrigerator compressors and electronics. HCFC-22, substitute of CFC-12 and mainly emitted from refrigeration units and air conditioning systems [*Aucott et al.*, 1999; *McCulloch et al.*, 2003], however, did not show a similar pattern to the CFCs, reflecting the fact that HCFC-22 and CFCs were not used within the same sources although they are all refrigerants, and/or their temporal patterns were influenced by the photochemical lifetime (i.e., HCFC-22: 11.8 years, and CFCs: 45–100 years). Moreover, CCl_4, usually used as feedstock for CFC and HCFC production and sometimes used as industrial solvent [*Altshuller*, 1976; *Sturrock et al.*, 2002], presented a different pattern from that of CFCs and HCFC-22, confirmed by the fact that CCl_4 correlated much more poorly with CFCs (R^2 = 0.26–0.37) than the CFCs did among themselves (R^2 = 0.62–0.68).

[21] Methyl chloride (CH_3Cl) and CH_3Br are emitted from both biogenic sources (i.e., oceans and plants) and anthropogenic sources such as biomass burning and biofuel use, including coal burning [e.g., *Blake et al.*, 1996; *McCulloch et al.*, 1999]. CH_3Cl is also commonly used as a solvent, processing agent and feedstock for chemical production in China [*Jiang*, 2004], whereas CH_3Br is used as a pesticide in Hong Kong (Hong Kong Environmental Protection Department (HKEPD), http://www.epd.gov.hk, 2007). Therefore, their distributions are more complicated than other purely anthropogenic halocarbons. Indeed, the temporal variations of CH_3Cl and CH_3Br were found to be different from CO (the tracer of combustion), CH_2Cl_2 (the marker of solvent) and CFC-12 (the tracer of refrigerant), reflecting the contribution of multiple sources to the methyl halides at the site (Figures 3a–3c).

[22] Though both HCFC-141b and HCFC-142b are the substitutes of CFCs and mainly used as refrigerants [*McCulloch et al.*, 2003], their temporal patterns were surprisingly different in the study region (R^2 = 0.03) (Figure 3d). Furthermore, used as fire extinguishers and being one of the most important anthropogenic sources of bromine atoms in the stratosphere [*Butler et al.*, 1998; *Montzka et al.*, 2003], H-1211 showed a different temporal pattern from that of H-2402 (R^2 = 0.06). It was also found that the temporal pattern of CFC-12 was significantly different from that of HCFC-141b (R^2 = 0.02) and HCFC-142b (R^2 = 0.10), implying their different industrial application and/or different emission patterns (Figures 3b and 3d).

3.1.2. Diurnal Variations of Halocarbons

[23] To better understand the temporal variations of halocarbons, we present the diurnal variations of halocarbons and other gaseous air pollutants from 6–8 November 2002, as an example (Figure 4). The maximum ozone mixing ratios reached 129 ppb, 203 ppb and 91 ppb on 6, 7, and 8 November 2002, respectively. It can be seen that there were no consistent diurnal variations for halocarbons, total nonmethane hydrocarbons and gaseous air pollutants. On 6 November, ambient TCFCs, THCFCs, solvent-related halocarbons, CH_3Cl, TVOCs, NO, SO_2, and CO remained at low levels, the ratios of *i*-butane/propane and *m*-xylene/ethylbenzene were 0.38 (R^2 = 1) and 0.12 (R^2 = 0.5), respectively, suggesting that the air masses were photochemically aged. On 7 November, the diurnal trend of TVOCs and TCFCs followed the pattern of primary pollutants such as SO_2, NO and CO, but it differed from that of O_3. The NO level was as high as 95 ppb, and the ratios of *i*-butane/propane and *m*-xylene/ethylbenzene were 0.47 (R^2 = 1) and 1.39 (R^2 = 0.9), respectively, suggesting that the air masses were affected by fresh emissions. The decrease in TVOCs with time suggests that TVOCs might participate in photochemical ozone formation in addition to atmospheric transport, whereas the decrease in the mixing ratios of TCFCs, which are longer-lived, could be mainly due to the atmospheric dispersion. The high halocarbon levels in the early morning were likely caused by the accumulation in the lower nighttime boundary layer and regional air masses on the basis of the analysis of source origins in section 3.2. However, the diurnal patterns of CH_3Cl, TCFCs and solvent-use-related halocarbons, which showed less diurnal variations, were different from TVOCs and other primary pollutants. On 8 November, the mixing ratios of all pollutants were back to lower levels except TCFCs and CH_3Cl, and the ratios of *i*-butane/propane and *m*-xylene/ethylbenzene reduced to 0.40 (R^2 = 0.95) and 0.31 (R^2 = 0.8), reflecting the aging of the air masses.

3.2. Regional, Local, and Marine Halocarbons in the Greater PRD

[24] On the basis of the results of Lagrangian particle release simulation (section 2.3), 27 of 188 samples had purely originated from the Hong Kong local area, 23 samples were predominantly from the inner PRD region and 19 samples were identified as marine air in origin. The rest of the samples were affected by a mix of local, regional and marine air.

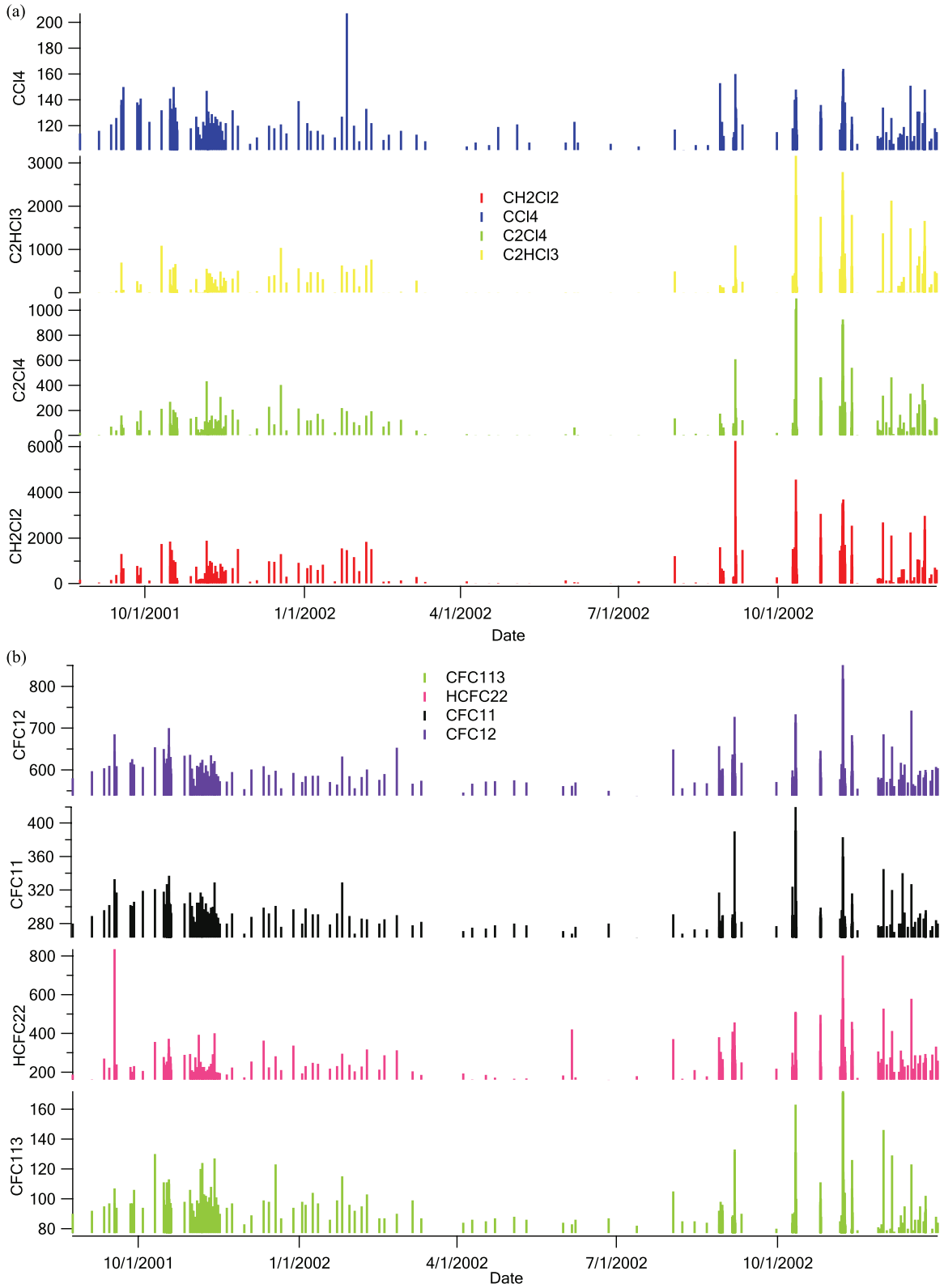

Figure 3. Time series of observations of (a) CH_2Cl_2, C_2Cl_4, C_2HCl_3, and CCl_4; (b) CFCs and HCFC-22; (c) CH_3Cl, CH_3Br, and CO; and (d) HCFC-141b, HCFC-142b, H1211, and H2402 at Tai O from August 2001 to December 2002. The *y* axis is mixing ratio in ppt except CO in ppb. A total of 188 whole air samples were collected, ranging from 1 to 32 samples per month.

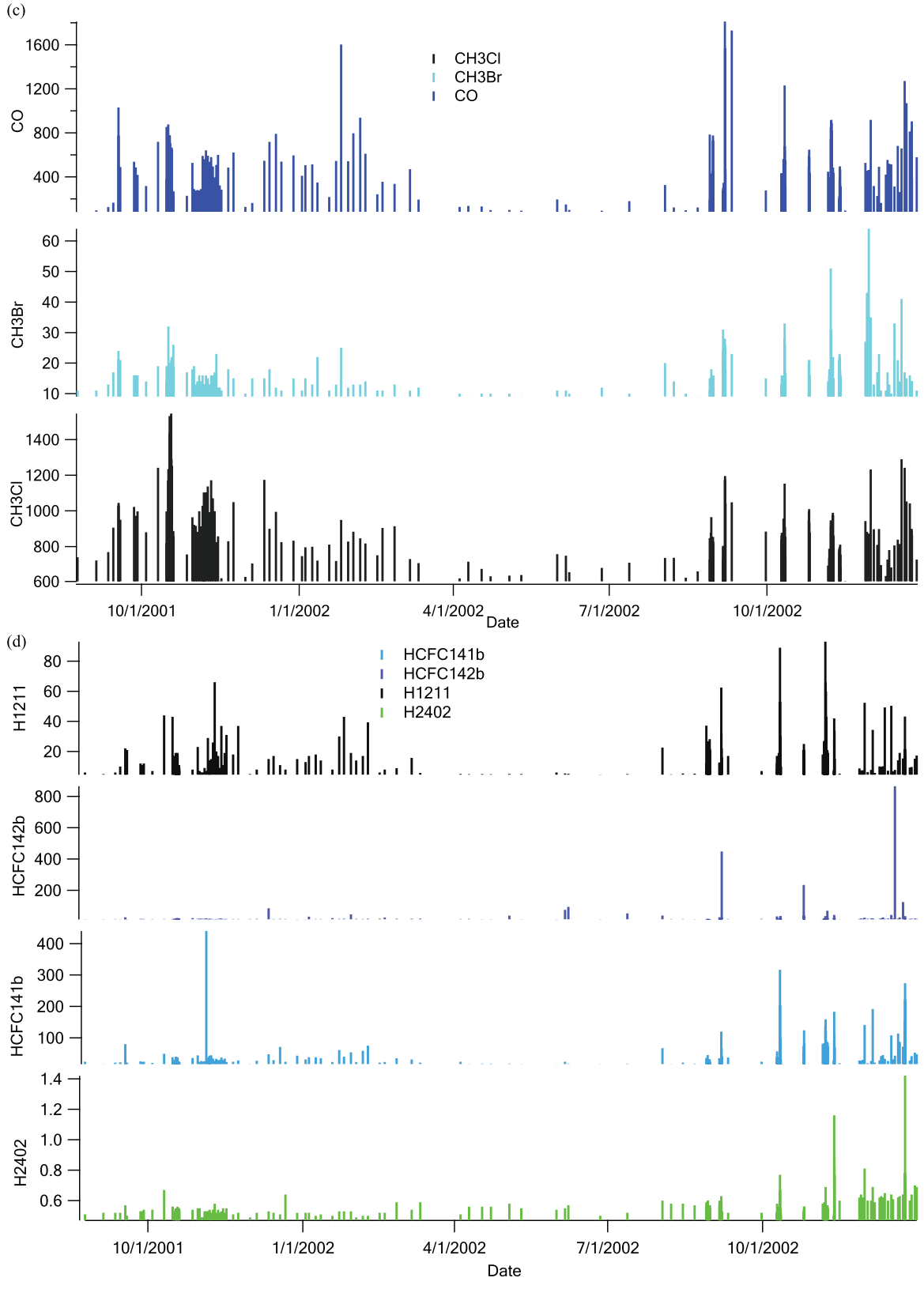

Figure 3. (continued)

Table 1. Mean Mixing Ratios of Halocarbons in the Inner PRD, Urban Hong Kong, and South China Sea, Together With Background Levels Extracted From TRACE-P Data, Estimated Global/Tropical Surface Mixing Ratios, and Inner PRD Levels Obtained by Another Study[a]

			Marine Air (n = 19)		Urban Air (n = 27)		Regional Air (n = 23)		TRACE-P		
Formula	Common Name	Lifetime	Mean (Standard Deviation)	Median	Mean (Standard Deviation)	Median	Mean (Standard Deviation)	Median	Background[b] (Standard Deviation)	Estimated Global Surface Level	Inner PRD[c]
CCl_2F_2	CFC-12	100 year	570 (7)	570	615 (17)	609	616 (17)	602	535 (1)	541 (5)[d]	538–973
CCl_3F	CFC-11	45 year	277 (3)	275	294 (7)	288	298 (11)	286	259 (1)	257 (4)[d]	259–1310
CCl_2FCClF_2	CFC-113	85 year	86 (2)	86	96 (6)	91	98 (7)	92	79 (1)	80 (1)[d]	117–291
$CHClF_2$	HCFC-22	11.8 year	199 (28)	173	322 (41)	297	304 (59)	249	151 (2)	145 (2)[d]	161–1970
CH_3CCl_2F	HCFC-141b	9.2 year	19 (1)	18	56 (13)	48	43 (13)	32	15 (0.4)	13.9 (0.5)[d]	13–76
CH_3CClF_2	HCFC-142b	18.5 year	24 (10)	16	32 (16)	20	18 (2)	17	14 (0.3)	12.9 (0.3)[d]	12–68
$CHCl_3$	Chloroform	3–5 months	18 (7)	13	43 (7)	44	104 (62)	73	9 (1)	11 (3)[d,e]	14–249
CCl_4	Carbon tetrachloride	35 year	110 (3)	107	121 (4)	120	122 (7)	115	99 (0.6)	95 (3)[d]	100–16000
CH_2Cl_2	Methylene chloride	3–5 months	72 (24)	61	948 (306)	856	1087 (558)	557	28 (4)	8 (1)[f]	154–6010
C_2HCl_3	Trichloroethene		5 (3)	3	465 (179)	405	260 (149)	76	0.4 (0.2)	0 (0)[f]	1.7–497
C_2Cl_4	Tetrachloroethene	2–3 months	17 (10)	7	167 (47)	155	117 (53)	65	5 (1)	4 (3)[d]	9.8–3590
CH_3Cl	Methyl chloride	1.3 year	679 (22)	675	940 (89)	872	899 (64)	847	535 (8)	525 (18)[f]	532–1090
CH_3Br	Methyl bromide	9–10 months	11 (1)	10	19 (4)	17	18 (2)	16	8 (0.2)	7.6 (0.2)[f]	9.4–23.2

[a]Ratios are in pptv.
[b]Lowest 25th percentile of airborne TRACE-P data collected below 1500 m [*Blake et al.*, 2003; *Barletta et al.*, 2006]. Standard deviation is with 95% confidence interval.
[c]Range from *Chan and Chu* [2007].
[d]Average mixing ratios summarized from data of AGAGE, NOAA/ESRL, and UCI global networks for year 2002 [*CDIAC*, 2005; *AGAGE*, 2008].
[e]Median tropical surface (<1 km) mixing ratio from data of TRACE-P [*Ko and Poulet*, 2003].
[f]Average mixing ratios from data of Cape Grim [*AGAGE*, 2008].

3.2.1. Comparison of Regional, Local, and Marine Halocarbon Sources

[25] Thirteen main halocarbons in the regional, local and marine samples were selected for comparison for the following reasons: their abundance in the atmosphere, their wide industrial and commercial use, and their ozone depletion potential. Table 1 shows their average mixing ratios for marine samples, Hong Kong urban samples, and inner PRD regional samples, together with background levels reported in literature. With the exception of HCFC-142b, the mixing ratios of all other halocarbons in marine air were significantly lower than those in urban and regional air ($p < 0.01$). In particular, the levels of short-lived species such as CH_2Cl_2, C_2HCl_3 and C_2Cl_4 showed large variations in the samples, and the median mixing ratios in urban/regional air were about 9–14, 25–135, and 9–22 times that in marine background air, respectively. This fact reflects their wide use in the greater PRD region and their short atmospheric lifetimes, which results in comparatively low concentrations in the aged marine air masses. These three species are often used as cleaning solvent and dry cleaning fluid in the PRD [*He et al.*, 2002; *Chan and Chu*, 2007]. Given the fact that the marine air is aged and far removed from continental emission sources, the marine (South China Sea) halocarbon mixing ratios can be considered as the PRD background. It was found that there was no difference of HCFC-142b mixing ratios between marine background and polluted urban/regional air. This may owe to the fact that HCFC-142b is a new chemical and is gradually replacing CFC-11 in industrial usage in the PRD [*Montzka et al.*, 1994; *Simmonds et al.*, 1998a; *Chan and Chu*, 2007]. HCFC-142b remains inside foam products, and minor leaking loss during the service life of the foam products leads to its steady emission into the atmosphere. Occasionally, a large increase in the local samples (1200–4700%) was observed in this study.

[26] All halocarbons in urban Hong Kong air did not show a significant difference from those in the inner PRD regional air (Table 1), reflecting the dominant impact of the greater PRD regional air on the halocarbon levels, as most halocarbons are still allowed to be used in China. It is noteworthy that although the mean mixing ratio of C_2HCl_3 in Hong Kong was about 1.8 times that in inner PRD, there was no statistical difference between Hong Kong and the inner PRD due to large variations of C_2HCl_3 in samples. Inspection of the air samples indicated that the mixing ratio of C_2HCl_3 in Hong Kong ranged from 1.4 to 1754 ppt, whereas it was between 18 and 1372 ppt in the inner PRD, reflecting inconsistent use of this halocarbon in the greater PRD. Although most industrial enterprises have moved to the inner PRD since 1980s, there are still some electronic industrial companies and dry cleaning facilities in Hong Kong, which often use C_2HCl_3 as a cleaning solvent. On the one hand, though Hong Kong is geographically a part of the greater PRD, it is actually a developed metropolis (Non-Article 5 party). Under the Montreal Protocol, the CFCs, halons, CCl_4 and CH_3CCl_3 in Hong Kong have been totally phased out by 1996, and CH_3Br has been strictly controlled for use only in local quarantine and preshipment applications since 1995. On the other hand, the consumption of HCFCs, the replacement of CFCs, has been frozen at the base level starting in 1996 (HKEPD, http://www.epd.gov.hk/epd/english/environmentinhk/air/data/phase_out.html, 2005, hereinafter referred to as HKEPD, 2005a).

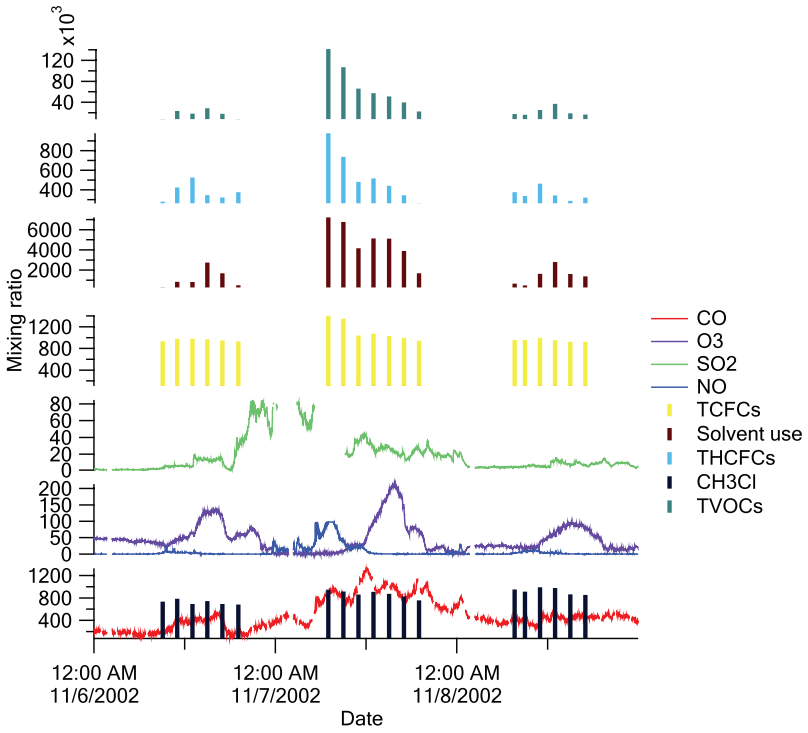

Figure 4. Diurnal variations of main halocarbons and other gaseous air pollutants on 6–8 November 2002. TCFCs = CFC-11 + CFC-12 + CFC-113; THCFCs = HCFC-22 + HCFC-141b + HCFC-142b; solvent use = CH_2Cl_2 + C_2HCl_3 + C_2Cl_4; TVOCs – 40 nonmethane hydrocarbons.

Because of the above, the total consumption of ozone depleting substances in Hong Kong has significantly decreased from 5540 tons in 1989 to 173 tons in 2002 (HKEPD, 2005a).

3.2.2. Comparison With Other Studies

[27] It is of interest to compare the background levels of halocarbons in the greater PRD with the estimated global surface mixing ratios and the TRACE-P background (Table 1). Here, the lower quartile of halocarbon mixing ratios measured at altitudes below 1.5 km during the airborne NASA GTE Transport and Chemical Evolution over the Pacific (TRACE-P) field campaign (February–April 2001) was used for comparison [*Blake et al.*, 2003; *Barletta et al.*, 2006]. The estimated global surface mixing ratios in Table 1 were based on three global ground-based measurement networks: Advanced Global Atmospheric Gases Experiment (AGAGE) network; the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) network; and the University of California at Irvine (UCI) network. In these networks, the global surface mixing ratios of ozone depleting substances are continuously monitored at multiple *in situ* and flask-sampling sites in very remote areas (e.g., Barrow, Alaska and Cape Grim, Tasmania) [*Carbon Dioxide Information Analysis Center* (CDIAC), 2005; *AGAGE*, 2008]. Estimated global surface mixing ratios in 2002 were used as a background for comparison. In addition, the global background level of $CHCl_3$ was obtained from the data (<1 km) of TRACE-P collected over the Western Pacific and the South China Sea (23.5°N to 8°N) in 2001 [*Ko and Poulet*, 2003].

[28] The average mixing ratios for all the halocarbons in the PRD background marine air were higher than the corresponding TRACE-P background and the global surface levels (Table 1). In contrast to long-lived species such as CFC-12, CFC-11, and CFC-113, which showed small difference (<10%) from the TRACE-P background/global surface levels, the rest of the halocarbons had significantly large differences (>10%). In particular, the difference for the very short-lived halocarbons, i.e., $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4, was notably large (39–100%), suggesting significant local and perhaps regional emissions in the greater PRD. Relatively large differences for HCFC-141b (21–26%) plus small differences for CFCs reflected the fact that CFCs are being gradually replaced by HCFCs in the greater PRD, and long-lived CFCs are more stable with better global mixing in the atmosphere.

[29] Comparing the measurement data in this study to the field campaign in the inner PRD in 2000 [*Chan and Chu*, 2007], we found that the average mixing ratios for almost all target halocarbons measured in inner PRD and urban Hong Kong fell into the range obtained in 2000 and on the lower side [*Chan and Chu*, 2007]. But it is difficult to conclude that the lower values observed in this study were related to the effects of the phase out, as the number of samples for both studies is not enough for such a conclusion. Instead, the relatively lower values of halocarbons in this study were partly attributed to the fact that our sampling site was about 50 km downwind of the inner PRD while the samples reported by *Chan and Chu* [2007] were collected inside the inner PRD and some were even close to emission sources. One exception was CFC-113. The mixing ratios in this study were lower than the minimum value (117 pptv) in 2000, probably reflecting the decreased use of CFC-113. In fact, in 1999 the Chinese government proposed that the total consumption of CFC-113 in China was to be 800, 600 and 500 ODP

Table 2. Measured Halocarbon: CO Relationships and Estimated Halocarbon Emissions[a]

	Inner PRD (n = 23)			HK (n = 27)		
	R^2	ΔX/ΔCO (pptv/ppbv)	Emission[b] (Gg a^{-1})	R^2	ΔX/ΔCO (pptv/ppbv)	Emission (Gg a^{-1})
CFC-12	0.40	0.054 ± 0.014[c]	1.5 ± 0.4	0.29	0.097 ± 0.030	0.05 ± 0.02
CFC-11	0.30	0.031 ± 0.010	1.0 ± 0.3	0.40	0.046 ± 0.011	0.03 ± 0.005
CFC-113	0.38	0.022 ± 0.006	0.9 ± 0.3	0.34	0.037 ± 0.010	0.03 ± 0.007
HCFC-22	0.15	0.115 ± 0.060	2.2 ± 1.2	0.15	0.167 ± 0.079	0.06 ± 0.03
HCFC-141b	0.28	0.035 ± 0.012	0.9 ± 0.3	0.45	0.093 ± 0.020	0.05 ± 0.008
$CHCl_3$	0.08	0.090 ± 0.066	2.4 ± 1.8	0.53	0.050 ± 0.009	0.03 ± 0.004
CCl_4	0.31	0.019 ± 0.006	0.7 ± 0.2	0.53	0.031 ± 0.0058	0.02 ± 0.004
CH_2Cl_2	0.62	2.236 ± 0.376	42.8 ± 7.2	0.35	1.865 ± 0.514	0.7 ± 0.2
C_2HCl_3	0.34	0.433 ± 0.134	12.8 ± 4.0	0.41	1.196 ± 0.285	0.7 ± 0.2
C_2Cl_4	0.53	0.194 ± 0.040	7.3 ± 1.5	0.28	0.26 ± 0.084	0.2 ± 0.06
CH_3Cl	0.56	0.244 ± 0.047	2.8 ± 0.5	0.53	0.68 ± 0.126	0.2 ± 0.03
Total			75.3 ± 8.7			2.1 ± 0.3

[a]The parameter n is the number of samples; R^2 is the Pearson correlation coefficient of ΔX/ΔCO; ΔX/ΔCO is the reduced major axis regression slopes (pptv/ppbv).
[b]The emission estimates are calculated using Δhalocarbon: ΔCO relationships measured in the study period, and a bottom-up emission inventory for anthropogenic CO in inner PRD and Hong Kong is used [*Streets et al.*, 2003; *CGRER*, 2007].
[c]Slope uncertainties are calculated by assuming the linear model.

tonnes in year 2000, 2001, and 2002, respectively [*State Environmental Protection Administration*, 2002].

3.2.3. Halocarbon Emission Estimates for Inner PRD and Hong Kong

[30] It would be extremely interesting if we could estimate the emissions of halocarbons using the field measurement data, and compare these estimated emissions with existing emission inventory data, such as reports from local government and reports in the literature like that of *Streets et al.* [2003]. In order to make quantitative estimates of emissions from the inner PRD and Hong Kong we used observed relationships between halocarbons and CO to determine the corresponding halocarbon emissions. Sources of CO from fuel consumption are relatively well known and are in general colocated with the halocarbon sources [*Palmer et al.*, 2003]. Halocarbons and CO both have background latitudinal gradients. We removed the influence of these gradients on the halocarbon:CO relationship by subtracting background values. Here the TRACE-P backgrounds in Table 1 are used for the halocarbons, and the lowest CO mixing ratio in the South China Sea air is defined as the CO background value. Table 2 shows the measured halocarbon: CO correlations and the estimated halocarbon emissions for inner PRD and Hong Kong. The CO emissions for the inner PRD and Hong Kong that were used for this calculation are 6385.52 tonnes and 217.41 tonnes, respectively [*Streets et al.*, 2003; *Center for Global and Regional Environmental Research* (CGRER), 2007]. The relatively weak $\Delta CHCl_3/\Delta CO$ correlation (R^2 = 0.08) for air masses originating from the inner PRD means that our corresponding emission estimate is highly uncertain. It is noteworthy that uncertainties on the halocarbon: CO slopes (Table 2) are calculated by assuming a linear model, and there are additional errors associated with this assumption that we do not take into account.

[31] Bearing these assumptions and uncertainties in mind, the total halocarbon emissions in the inner PRD were very much higher than those in Hong Kong (Table 2), reflecting different control requirements between Article 5 and Non-Article 5 parties under the Montreal Protocol. Our total halocarbon emission estimate for inner PRD (75.3 ± 8.7 Gg a^{-1}) is ~80% larger than the value (16.04 Gg a^{-1}) given by *Streets et al.* [2003], highlighting serious shortcomings in our knowledge of the halocarbon sources in inner PRD. On the other hand, the total halocarbon emission estimate for Hong Kong (2.1 ± 0.3 Gg a^{-1}) is in good agreement with emission estimated by *Streets et al.* [2003] (3.2 Gg a^{-1}), but is much higher than the bottom-up estimate (0.165 Gg a^{-1}) by the Hong Kong Government (HKEPD, 2005a).

[32] Among the target halocarbons in inner PRD and Hong Kong, the estimated emissions of CH_2Cl_2, C_2HCl_3 and C_2Cl_4 accounted for about 80–84% of the total emission, suggesting a significant contribution to ambient halocarbons from solvent use by electronic and textile industries in the study region. The estimated CFC emissions (3.4 ± 0.6 Gg a^{-1} for the inner PRD and 0.1 ± 0.02 Gg a^{-1} for Hong Kong) were similar to those of HCFCs (3.2 ± 1.2 Gg a^{-1} for the inner PRD and 0.1 ± 0.03 Gg a^{-1} for Hong Kong). Interestingly, the estimated $CHCl_3$ emission in the inner PRD was 2.4 ± 1.8 Gg a^{-1}, which was approximately 100 times that in Hong Kong (0.03 ± 0.004 Gg a^{-1}), implying more widespread use in the inner PRD.

[33] In order to obtain a more detailed picture of halocarbons in the study region, we focus on the source profiles and source apportionments of halocarbons in the greater PRD region obtained from the PMF receptor model.

3.3. Identified Source Profiles of Halocarbons in the Greater PRD Region

[34] On the basis of the air mass classification in section 2.3, 112 of the 188 samples were identified as samples which were not affected by marine air. The 112 samples included 27 Hong Kong samples and 23 inner PRD samples. To ensure the statistical power of the PMF modeling and to obtain robust modeling results, we performed PMF modeling on the 112 continental samples. Eleven main halocarbons were selected for the analysis since they are the most abundant parameters and/or are typical tracers of various emission sources. In order to understand the contribution of biomass/biofuel and coal burning, the combustion marker of CO was also included in the PMF modeling. Different from other pollutants, halocarbons, both long-lived and short-lived species, have significant contributions from global and regional background levels, even though the air masses are proven to originate from urban areas. This has been well demonstrated

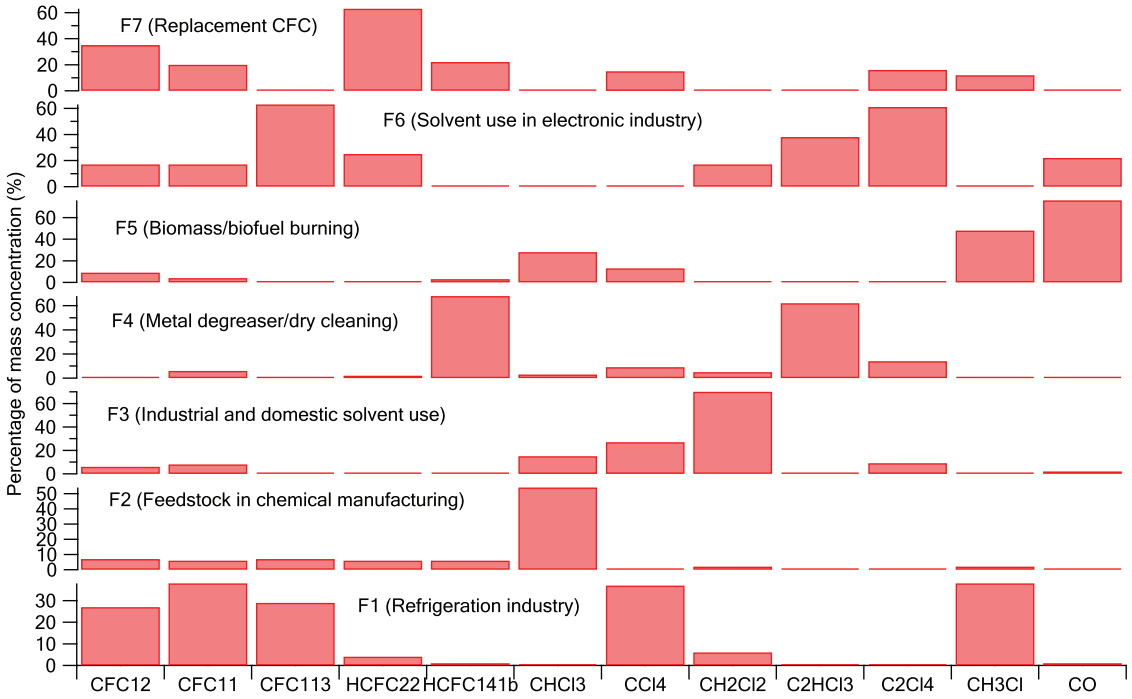

Figure 5. Source profiles resolved from PMF in the greater PRD.

in the comparison between the measured values and regional/global background levels (section 3.2.2). Hence, we present a PMF model run in which the influence of these background levels on the measured halocarbons has been removed by subtracting background values. The deducted background values are the TRACE-P backgrounds in Table 1. After running the PMF model, seven sources were identified in the greater PRD (Table 3 and Figure 5).

[35] The first source was an industrial source related to refrigerant production, which is characterized by a high mass percentage of three CFCs, as well as CCl_4 and CH_3Cl. As mentioned in section 3.1, CFCs are mainly used as refrigerants in cooling appliances and air conditioning [*Aucott et al.*, 1999; *McCulloch et al.*, 2001, 2003; HKEPD, 2005a], whereas CCl_4 is mainly used as feedstock for CFC production [*Altshuller*, 1976; *Sturrock et al.*, 2002]. The high correlation between CCl_4 and CFCs suggests that this source was more related to the production than the consumption of refrigerants. On the other hand, a high contribution of CH_3Cl to this source (~38%) suggests that CH_3Cl was also related to the production of refrigerants or had similar emission patterns, apart from the biomass/biofuel and/or coal burning (source five) in this region. It has been reported that CH_3Cl has a dominant source of vegetation and is also emitted from ocean in tropical coastal regions [e.g., *Warneck*, 2000; *Youkouchi et al.*, 2000]. However, no significant correlation between CH_3Cl and the biogenic tracer, nor between CH_3Cl and the oceanic tracer dimethyl sulfide (DMS) was found during the study period (R^2 = 0.007 and 0.04, respectively), suggesting that vegetation and oceans are not the sources of CH_3Cl in the greater PRD region. Indeed, CH_3Cl used to be a widely used refrigerant, but because of its toxicity this use has been discontinued. It might also be used as a cleaning solvent in the production processes of refrigerants in China [*Jiang*, 2004]. The results reveal that about 40% of the CH_3Cl in the greater PRD originated from industrial usage.

Table 3. Source Profiles of Halocarbons in the Greater PRD Region[a]

	F1	F2	F3	F4	F5	F6	F7
CFC-12	17.8	4.4	4.1	0.0	5.8	11.4	23.2
CFC-11	12.4	2.1	2.5	1.9	1.4	5.6	6.6
CFC-113	4.7	1.2	0.0	0.0	0.0	10.2	0.0
HCFC-22	5.0	7.4	0.0	2.0	0.0	30.3	76.0
HCFC-141b	0.2	1.7	0.0	19.6	0.7	0.0	6.4
$CHCl_3$	0.0	23.4	6.4	1.4	12.4	0.0	0.0
CCl_4	7.7	0.0	5.5	1.8	2.7	0.0	3.0
CH_2Cl_2	52.9	16.7	574.9	41.3	0.0	138.5	0.0
C_2HCl_3	0.0	0.0	0.0	213.7	0.0	131.4	0.0
C_2Cl_4	0.0	0.0	11.0	16.2	0.0	71.3	19.3
CH_3Cl	135.3	7.6	0.0	0.0	168.1	0.0	41.4
CO (ppb)	3.2	0.0	7.8	0.0	366.6	103.6	0.0
Sources	refrigeration industry	feedstock in chemical manufacturing	industrial and domestic solvent use	metal degreaser/ dry cleaning	biomass/biofuel burning	solvent use in electronic industry	replacement CFCs

[a]Profiles are in ppt; n = 112.

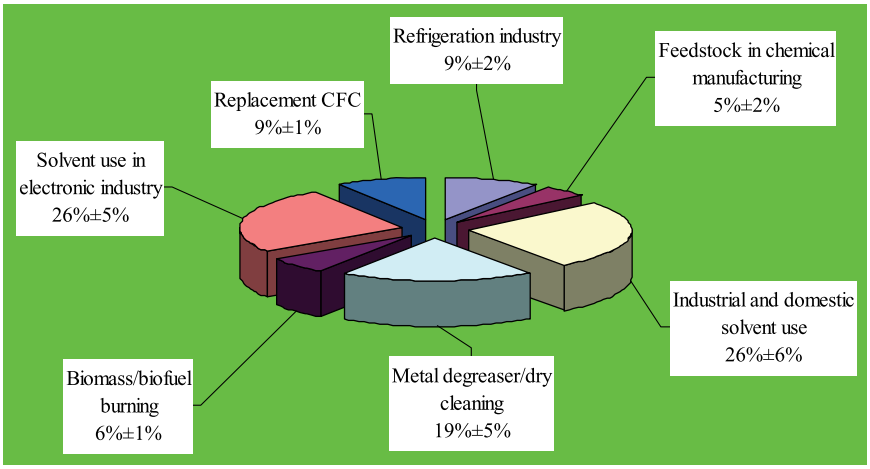

Figure 6. Source contributions to the total halocarbons in greater PRD (mean ± standard error).

[36] A high percent of $CHCl_3$ mass concentration (54%) was found in source two, whereas other halocarbons made negligible contributions to this source. $CHCl_3$ is used as a feedstock in chemical manufacturing, mainly to produce HCFC-22 [*Simmonds et al.*, 1998b; *Aucott et al.*, 1999]. In China, about 75% of $CHCl_3$ is consumed by the production of HCFC-22, followed by the pharmaceutical industry [*Jiang*, 2004].

[37] The third source was solely distinguished by the contribution of about 70% from CH_2Cl_2, which is well known as a feedstock for foam plastic products, metal cleaning and other solvent uses [*Cox et al.*, 2003]. *Chan and Chu* [2007] found that the spatial variation of CH_2Cl_2 was different from those of C_2HCl_3 and C_2Cl_4 in inner PRD, because both C_2HCl_3 and C_2Cl_4 are used as industrial cleaning solvents that are not commonly used for retail and commercial purposes, whereas CH_2Cl_2 is used in more industrial and domestic activities. In China, CH_2Cl_2 is mainly consumed in plastic film production (50%), the pharmaceutical industry (20%), and in cleaning solvent use and chemical production (20%) [*Jiang*, 2004]. In addition, our study shows that small percentages of CCl_4 and $CHCl_3$ are assigned to source three, reflecting that some CCl_4 and $CHCl_3$ were used as solvents in the greater PRD. It is most likely that CCl_4 was used in both the inner PRD and Hong Kong, while $CHCl_3$ was mainly used in Hong Kong. This can be verified by the fact that $CHCl_3$ correlated fairly well with CH_2Cl_2 in Hong Kong but not in the inner PRD (see sections 3.4.2 and 3.4.4).

[38] The fourth source was distinguished by high mass percentages of HCFC-141b (68%) and C_2HCl_3 (62%). HCFC-141b has been widely employed as a replacement for CFC-11 as a foam blowing agent in the manufacture of rigid polyurethane foams for insulation purposes, and in the manufacture of integral skin foams for soles of shoes and motor vehicle dashboards and steering wheels [*Derwent et al.*, 2007]. It has also been used as a solvent for lubricants, coatings, and cleaning fluids for aircraft maintenance and electrical equipment [*Derwent et al.*, 2007]. In addition, C_2HCl_3 is mainly used as a degreasing solvent in electronic and textile industries [*Simmonds et al.*, 2006]. In the greater PRD, it is substantially used in manufacturing industries especially in the electronics industry as a cleaning solvent [*He et al.*, 2002; *Chan and Chu*, 2007]. In Hong Kong, there are numerous laundries mainly located in residential premises. Two types of dry-cleaning machines have been used in Hong Kong: vented and nonvented. Before the prohibition of vented dry cleaning machines in November 2006, about one third to one half of the existing dry-cleaning machines were the vented type, which meant that they released C_2HCl_3 vapor directly into the atmosphere during the drying cycle (HKEPD, http://www.epd.gov.hk/epd/english/environmentinhk/air/guide_ref/wn8_dry_info.html, 2005). Thus, we identified this source as metal degreasing and dry cleaning agents.

[39] The fifth source was characterized by a high mass percentage of CO (76%), indicating this source is related to the combustion source. Further inspection found that CH_3Cl made about 48% contribution to the source, suggesting the strong influence of biomass/biofuel and/or coal burning of this source [e.g., *Blake et al.*, 1996; *McCulloch et al.*, 1999].

[40] It can be seen that 63% of CFC-113, 61% of C_2Cl_4, and 38% of C_2HCl_3 originated from the sixth source. CFC-113 is particularly used as a cleaning agent in the electronic industry (HKEPD, 2005a), whereas C_2HCl_3 and C_2Cl_4 are used primarily as surface degreasing agents and dry cleaning fluids [*Simmonds et al.*, 2006]. In inner PRD cities, in particular in Dongguan, a city with many light industries (e.g., electronic computers, peripherals, and soldering machinery (Hong Kong Trade Development Council, http://www.tdctrade.com/mktprof/china/prd.htm, 2006)), C_2Cl_4 is widely used as an industrial cleaning solvent. This source was more likely related to solvent use in the electronic industry.

[41] The last source was specified with a high mass percentage of HCFC-22 (63%). HCFC-22, substitute of CFC-12, is mainly emitted from refrigeration units and air conditioning systems [*Aucott et al.*, 1999; *McCulloch et al.*, 2003]. In addition, about 35% of CFC-12 contributed to this source, indicating that the source is related to refrigeration, which is dominated by the substitute of CFC refrigerants. We classified this source as the replacement of CFCs.

3.4. Source Apportionment of Total Halocarbons in the Greater PRD

[42] The average contributions of each source to the total halocarbons in the greater PRD are illustrated in Figure 6. It can be seen that the use of solvent made the most significant contribution to the total halocarbons in the region (in total 71 ± 9% (mass percentage ± standard error percentage), of

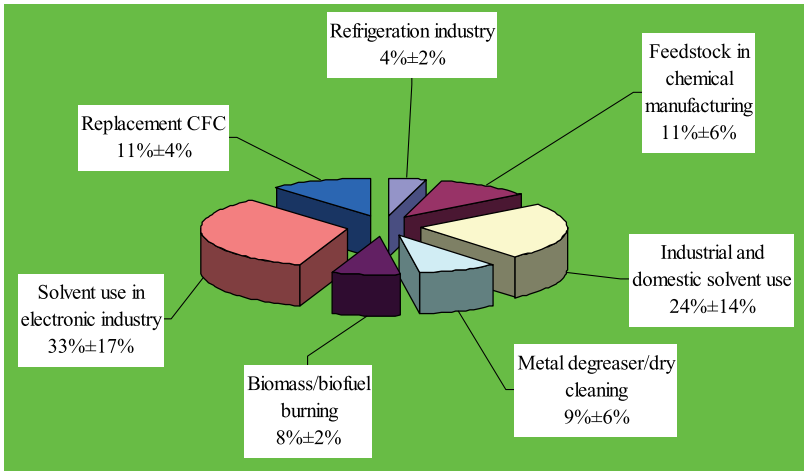

Figure 7. Source apportionments of the total halocarbons in inner PRD (mean ± standard error).

which was 26 ± 6% for mixed use of industrial and domestic solvent use; 26 ± 5% was for cleaning solvent in the electronic industry; and 19 ± 5% was for metal degreasers/dry cleaning), whereas refrigeration industry was the second largest contributor (in total 18 ± 2%, of which was 9 ± 2% for refrigeration industry; and 9 ± 1% for the replacement of CFCs). In addition, feedstock in chemical manufacturing contributed 5 ± 2% to the total halocarbons, and biomass/biofuel burning contributed 6 ± 1%. The estimate of biomass/biofuel burning was much lower than that (25%) estimated by *Guo et al.* [2006]. This is due to the fact that the contribution of biomass/biofuel burning by *Guo et al.* [2006] was based on total nonmethane volatile organic compounds (NMVOCs) with only two halocarbons (e.g., CH_3Cl and C_2Cl_4) included; and the emission of CH_3Cl was fully assigned to biomass/biofuel burning by *Guo et al.* [2006].

[43] The model-derived mixing ratios of individual halocarbons are compared with the corresponding species measured during the study period (not shown here). The modeled values are close to the measured halocarbon mixing ratios. The model underestimated the halocarbon levels by a range of 3% for CH_2Cl_2 and C_2HCl_3 to 20% for HCFC-141b [Uncertainty = $(\text{Halocarbon}_{\text{measured}} - \text{Halocarbon}_{\text{modeled}})/\text{Halocarbon}_{\text{measured}}$], suggesting that the PMF model is able to provide reasonable estimates of source apportionments of halocarbons in this study.

3.4.1. Source Distributions of Halocarbons in the Inner PRD

[44] As mentioned in section 3.3, within the 112 greater PRD samples, 23 samples were categorized as inner PRD air samples, which mean that these samples were not affected by urban Hong Kong. Hence, the source contributions of these 23 samples to the total halocarbons can be extracted from the 112 samples and then be averaged. In this way, the source apportionments of halocarbons in inner PRD can be explored (Figure 7).

[45] It can be seen that the contribution of the refrigeration industry decreased from 9 ± 2% in the greater PRD to 4 ± 2% in the inner PRD, and the use of solvents as metal degreasers and dry cleaning fluids decreased from 19 ± 5% to 9 ± 6%. In contrast, the contribution of feedstock in chemical manufacturing increased from 5 ± 2% in the greater PRD to 11 ± 6% in the inner PRD, and the use of cleaning solvent in electronic industry rose from 26 ± 5% to 33 ± 17%. Nevertheless, there were no significant variations for other sources. The contribution of the solvent use was the highest in the inner PRD (in total 66 ± 23%), followed by the refrigeration industry (in total 15 ± 4%) and feedstock in chemical manufacturing (11 ± 6%).

3.4.2. Interspecies Correlations in Inner PRD Region

[46] To further understand the source characteristics of halocarbons, scatter plots of main halocarbons in the inner PRD are presented in Figure 8a. Excellent correlation between CH_2Cl_2 and C_2Cl_4 was found in the inner PRD (R^2 = 0.96), and CH_2Cl_2 had good correlation with C_2HCl_3 (R^2 = 0.62). High correlations of CH_2Cl_2 with C_2Cl_4 and C_2HCl_3 imply these three halocarbons were emitted from same sources, i.e., solvent use or used in same patterns in inner PRD, in particular for CH_2Cl_2 and C_2Cl_4, and had similar sink behavior because of their similar lifetimes. Despite their different atmospheric lifetimes it can be seen that CH_2Cl_2 had some correlation with CCl_4 (R^2 = 0.45) and poor correlation with $CHCl_3$ (R^2 = 0.23), suggesting a solvent contribution to the mixing ratio of CCl_4, in contrast to $CHCl_3$ which was not of solvent origin in the inner PRD.

[47] Mainly used as refrigerant, CFC-12 was found to have good correlations with CFC-11 (R^2 = 0.82), and fair correlation with CFC-113 (R^2 = 0.59), HCFC-22 (R^2 = 0.55), and CCl_4 (R^2 = 0.60) in the inner PRD (Figure 8a), indicating similar sources or use patterns of these halocarbons. It is well known that CFCs are often used as refrigerants whereas HCFC-22 is a substitute of CFC-12 [*Aucott et al.*, 1999; *McCulloch et al.*, 2003], and CCl_4 is mainly used as feedstock for CFC and HCFC production [*Altshuller*, 1976; *Sturrock et al.*, 2002]. There was some correlation between CFC-12 and CH_3Cl in the inner PRD (R^2 = 0.48), suggesting that some CH_3Cl use was related to cooling appliances and air conditioning systems. Formerly, CH_3Cl was a widely used refrigerant, but because of its toxicity this use has been discontinued.

[48] In addition, CH_3Cl had good correlations with the biomass/biofuel burning markers of CO (R^2 = 0.56) and CH_3Br (R^2 = 0.74), reflecting the contribution of biomass/biofuel burning in the inner PRD. Satellite data and our field observations have demonstrated the significance of biomass/biofuel combustion in the inner PRD, especially in autumn

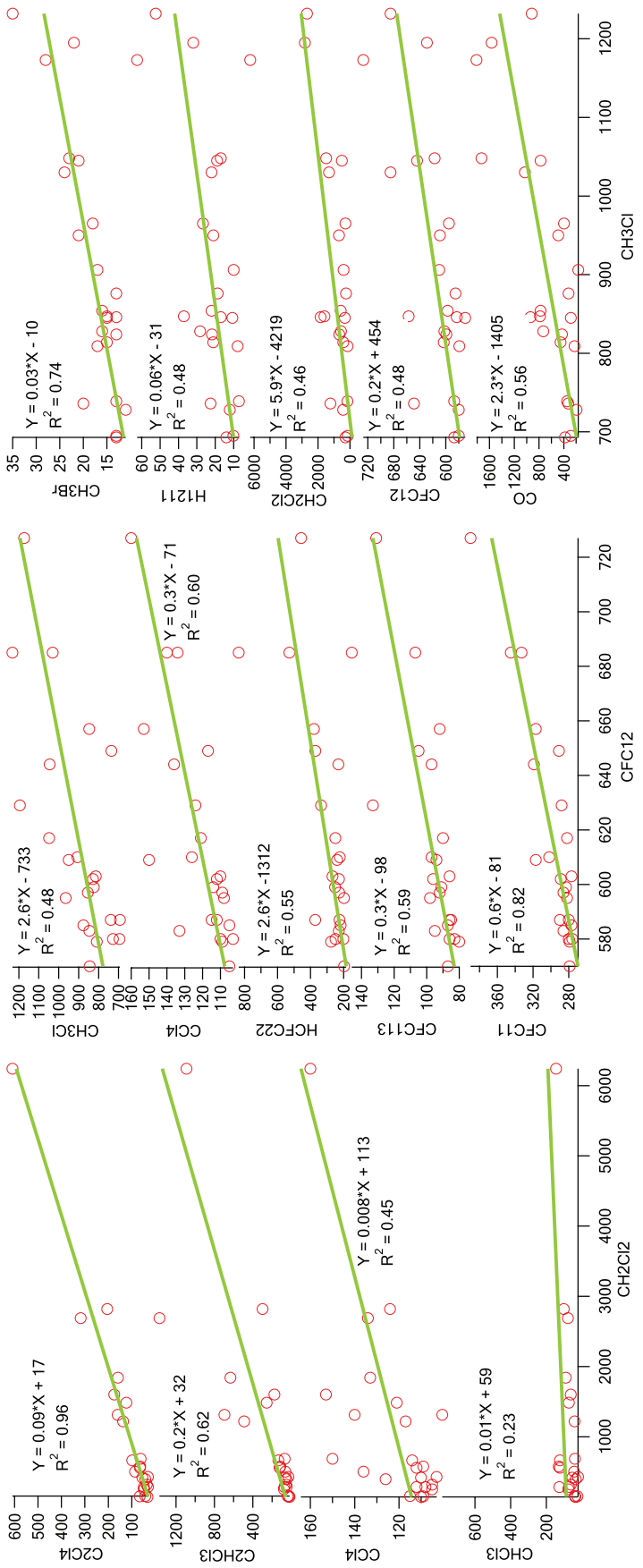

Figure 8. Correlations among halocarbons (a) in inner PRD and (b) in Hong Kong. The regressions with CH_3Cl in Figure 8a are heavily weighted to the low end.

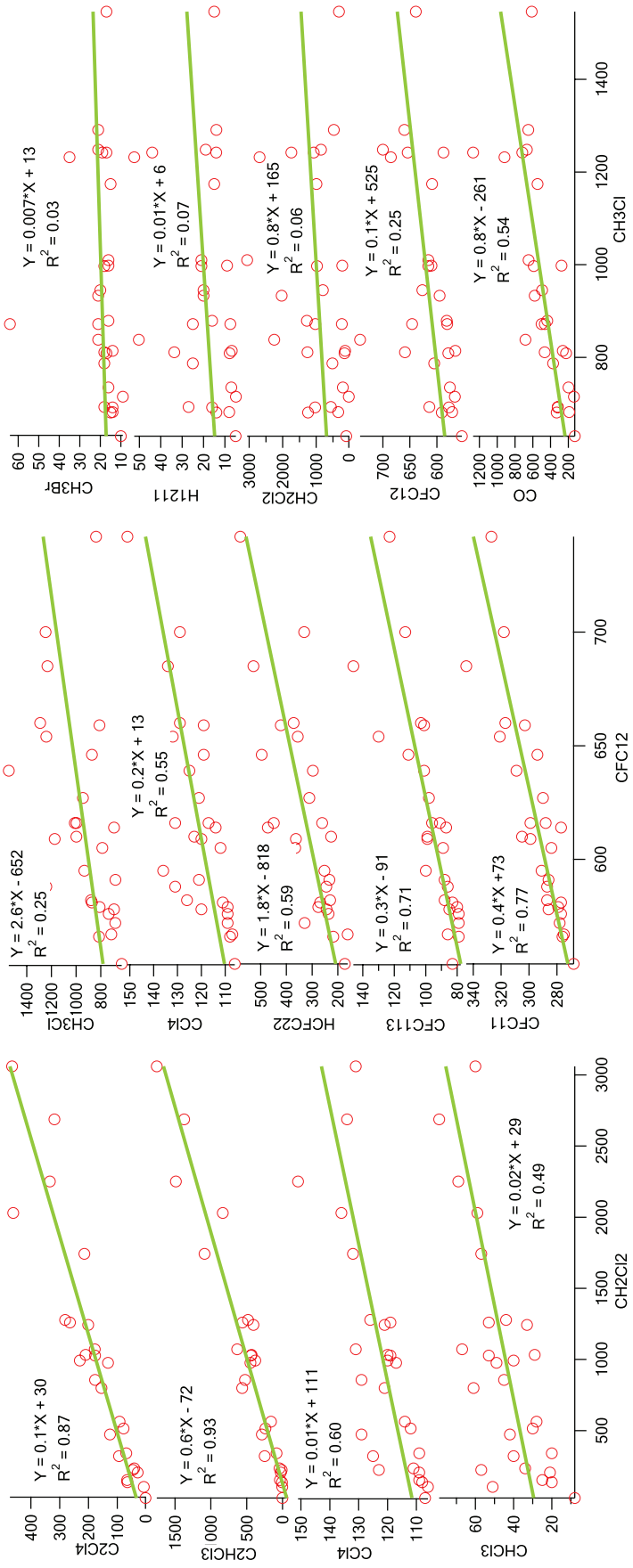

Figure 8. (continued)

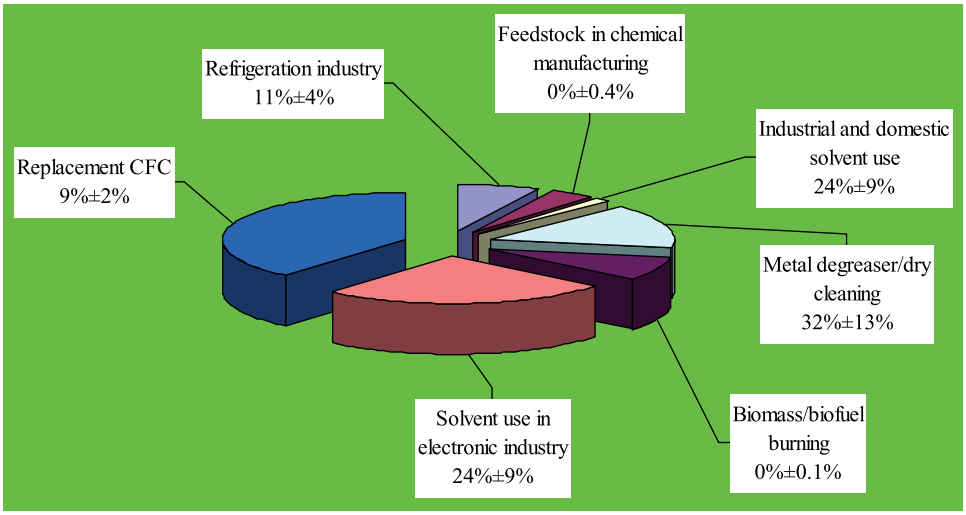

Figure 9. Source apportionments of the total halocarbons in Hong Kong (mean ± standard error).

[*Guo et al.*, 2006]. Furthermore, coal burning is the major energy source in the inner PRD and hence its contribution to ambient CH_3Cl and CH_3Br could be significant as well. Apart from its use as a refrigerant and its emission from biomass/biofuel burning, CH_3Cl also showed some correlation with CH_2Cl_2 ($R^2 = 0.46$) and H-1211 ($R^2 = 0.48$) in the inner PRD, suggesting that CH_3Cl was also used as a solvent and as aerosol propellants in the inner PRD.

3.4.3. Source Distributions of Halocarbons in Hong Kong

[49] Similar to the approach used in section 3.4.1, the source apportionments of halocarbons in Hong Kong were obtained from the 27 Hong Kong air samples (Figure 9). It was found that the emission sources of halocarbons in Hong Kong were relatively simple and only two major sources made contributions. About 80 ± 18% of the total halocarbons in Hong Kong were attributed to the use of solvents, of which, 24 ± 9% was caused by the mixed use of industrial and domestic solvent; 24 ± 9% from cleaning solvent use in the electronic industry; and 32 ± 13% from metal degreasers and dry cleaning. Emissions from refrigeration accounted for 20 ± 4% of the total halocarbons. The feedstock in chemical manufacturing and biomass/biofuel burning made negligible contributions to ambient halocarbon levels in Hong Kong.

[50] Comparing the source contributions in Hong Kong with that in the inner PRD, it was found that solvent use and the refrigeration industry were the common two sources of halocarbons in both the inner PRD and Hong Kong. However, the usage pattern of the solvent was substantially different: in Hong Kong much more solvent was used as metal degreasers and dry cleaning agents (32 ± 13% versus 9 ± 6%). Although the contribution of the HCFC related refrigeration was similar in both areas, the contribution of the CFC related refrigeration in Hong Kong was statistically higher than that in the inner PRD (11 ± 4% vs. 4 ± 2%), verifying the fact that many old CFC-containing refrigeration units and air conditioning systems were still in operation in Hong Kong during 2001–2002. The significant difference in halocarbon sources between the inner PRD and Hong Kong was the contributions from biomass/biofuel burning and the feedstock in chemical manufacturing, which made remarkable contributions to ambient halocarbon levels in the inner PRD, but was negligible in Hong Kong. This is consistent with the "zero" emission of biomass/biofuel burning estimated by *Streets et al.* [2003], and the fact that no industrial activities related to chemical manufacturing remained in Hong Kong.

3.4.4. Interspecies Correlations in Hong Kong

[51] In Hong Kong, excellent correlations were found between CH_2Cl_2 and C_2HCl_3 ($R^2 = 0.93$), and CH_2Cl_2 and C_2Cl_4 ($R^2 = 0.87$), whereas CH_2Cl_2 had good correlation with CCl_4 ($R^2 = 0.60$) and some correlation with $CHCl_3$ ($R^2 = 0.49$) (Figure 8b). High correlation coefficients among these halocarbons suggest that they had originated from similar sources in Hong Kong. In particular, the correlation coefficients between CH_2Cl_2 and CCl_4, and between CH_2Cl_2 and $CHCl_3$ in Hong Kong were higher than those in the inner PRD, implying that CCl_4 and $CHCl_3$ were more likely used as solvents in Hong Kong than in the inner PRD.

[52] Good correlations were also found among CFCs and HCFCs in Hong Kong, and they are mainly used as refrigerants [*Aucott et al.*, 1999; *McCulloch et al.*, 2003] (Figure 8b). It also can be seen that CFC-12 showed some correlation with CCl_4 ($R^2 = 0.55$) in Hong Kong. Unlike that in the inner PRD, poor correlation between CFC-12 and CH_3Cl ($R^2 = 0.25$) was found in Hong Kong, revealing that CH_3Cl in Hong Kong was not associated with cooling appliances and air conditioning.

[53] To further understand the potential sources of CH_3Cl in Hong Kong, scatter plots between CH_3Cl and CO, CH_2Cl_2, H-1211, and CH_3Br are shown in Figure 8b as well. Only good correlation between CH_3Cl and CO was identified ($R^2 = 0.54$), suggesting the combustion sources of CH_3Cl. It is well known that CH_3Cl is emitted from biomass/biofuel burning [e.g., *Blake et al.*, 1996; *McCulloch et al.*, 1999]. However, there was no major biomass burning in Hong Kong during the sampling campaign, but power plants in Hong Kong have been using coal as their main fuel. Hence, CH_3Cl in Hong Kong is believed to be released from coal burning. Interestingly, no correlation between CH_3Cl and CH_3Br ($R^2 = 0.03$)

was found in Hong Kong, implying that CH_3Br did not originate from coal burning in Hong Kong. In fact, CH_3Br is mainly used as pesticide in Hong Kong (HKEPD, 2007).

4. Summary and Conclusions

[54] In this study, we analyzed a comprehensive data set of halocarbons collected at a polluted rural/coastal site in southern China. The bulk air samples were classified into inner PRD, urban Hong Kong, continental China and marine air masses on the basis of Lagrangian particle release simulation. A PMF receptor model was applied to the classified samples of inland halocarbons to identify the major sources of halocarbons and to estimate the source contributions to halocarbon mixing ratios in the greater PRD region. Results indicate that there was no statistical difference between corresponding regional and local halocarbons, reflecting the dominant impact of regional air on the greater PRD halocarbon levels. Comparison shows that the average mixing ratios for all the halocarbons in the PRD background marine air were higher than the corresponding TRACE-P background and the global surface levels. In addition, various temporal patterns for different halocarbons in regional and local scales suggest their different use patterns and emissions and/or possibly different sink-driven effects. Seven source profiles were extracted from the PMF modeling, which indicated that solvent use dominated the distribution of halocarbons, followed by the refrigeration in both the inner PRD and Hong Kong. In Hong Kong more solvent was used as metal degreasers and dry cleaning agents than in the inner PRD. In addition, the contributions of feedstock in chemical manufacturing and of biomass/biofuel burning were negligible in Hong Kong.

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A. J. Ding, T. M. Fu, H. Guo, W. T. Hung, Y. S. Li, and T. Wang, Department of Civil and Structural Engineering, Hong Kong Polytechnic University, Kowloon, Hong Kong. (ceguohai@polyu.edu.hk)

B. Barletta, D. R. Blake, S. Meinardi, F. S. Rowland, and I. J. Simpson, Department of Chemistry, University of California, Irvine, CA 92697, USA.

S. M. Saunders, School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, Perth, WA 6009, Australia.